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クーロン３体系の束縛エネルギーに対して半古典量子化を行った。クーロン相互作用系は古典力学的スケール変換不変性をもつ。このスケール不変性を半古典波動関数ならびに相関関数に導入した。その結果、１本の古典軌道が大きさの階層が異なる自分自身の無限個のコピーと効果的に干渉をおこすことによりエネルギーが量子化されることがわかった。現在までに、２次元 H_2^+ の振電基底状態に近いエネルギーが算出されている。

1 Background of our research

We have been studying the all-particle dynamics of $H_2^+(p^+p^+e^-)$ and its muon substitution of electrons $(p^+p^+\mu^-)$ using semiclassical theory. The purposes of this work are, (i) to examine the validity of the Bron-Oppenheimer approximation, (ii) to obtain a deeper understanding of chemical bonding, and (iii) to investigate the applicability of semiclassical theory to systems having electrons. Primary target is simultaneous quantization of vibronic states of H_2^+.

In the problem of the energy quantization of Coulomb three-body systems, two main difficulties appear related to classical-quantum correspondence. (1) The problem of the energy quantization of chaos. Coulomb three-body system becomes strongly chaotic very easily. The quantization of the energy spectrum for a classically chaotic system has long been one of the central subjects in quantum mechanics and chaos theory. We still do not have a "perfect" semiclassical methodology that can be applied to many-body systems. (2) The root search for bounded classical trajectories. Because of swing-by motion of electron and the repulsive force between two protons, not all the trajectories are bounded to make H_2^+ molecule even in to-be-quantized energy region.

In a situation mentioned above, how can H_2^+ be quantized to have strong chemical bonding? In this work we show the way to overcome those difficulties by using a practically powerful method for the energy quantization of multi-dimensional systems and making use of scale invariance of Coulomb potential.

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2 Semiclassical methods

Starting point of our semiclassical methods is the Maslov type wave function, $\Psi(q,t) = F(q,t)\exp[(i/\hbar)S_{cl}]$, where S_{cl} denotes the solution of the classical Hamilton-Jacobi equation and F is a complex-valued function to be determined. Substitution of this wave function to the time-dependent Schrödinger equation leads to the equation of motion for function F. After some calculation, semiclassical wave function labeled by the initial momentum of classical trajectories is obtained, which is called Action Decomposed Function (ADF) [1].

If we consider an autocorrelation function of $C_{p_0}(-t,t) = \langle\Psi_{p_0}(-t)|\Psi_{p_0}(t)\rangle$ with ADF (p_0 denotes the initial momentum which labels ADF), we are able to obtain the Amplitude-Free Quasi-Correlation Function type II (AFC-II),

$$\tilde{C}_{II}(0,t) = \int dq_0 \left|F(q_t,0)\,F(q_0,0)\right| \exp\left[\frac{i}{\hbar}S_1(q_t,q_0,t) - i\frac{\pi}{2}M(q_0,q_t)\right] \tag{1}$$

where S_1 is the action and M is the Maslov index, both calculated along a set of classical trajectories. In this quasicorrelation function, contribution of weakly periodic turn-back orbit, whose initial momentum is $p_0 = 0$, is effectively taken. AFC-II does not include an amplitude factor as $|\partial q_t/\partial q_0|^{1/2}$, which diverges in the calculation of strongly chaotic systems and deteriorates the accuracy of numerical calculation. Therefore this is extremely powerful in the practical energy quantization of chaotic systems. Details on the AFC-II are shown in Ref. [2].

Let us consider a case where semiclassical methods are applied to a classically scale invariant system such as Coulombic system. Such a system has potential energy function of k-th homogeneous polynomial, $U(\alpha\vec{x}) = \alpha^k U(\vec{x})$, where $\vec{x}$ is the relevant coordinate and α is the scaling parameter. In Coulombic cases k equals -1. If a simultaneous scaling $q \to \alpha, t \to \alpha^{1-k/2}$ is carried out, a perfect copy of the original trajectory is given in the extended phase space, with other physical quantities transformed by some power of α appropriately. Now if the complete set of trajectories could be sampled in practical calculation of semiclassical wave functions and/or semiclassical autocorrelation functions, the resultant spectrum should not depend on the scaling parameter α. However, the reality is far from this ideal situation as indicated in Sec. I. So we consider taking classical scale invariance in semiclassical wave functions.

Integrateing ADF at the scale of α over the scaling parameter α yields a scale invariant semiclassical wave function. In a simlar fashion, a scale invariant quasicorrelation function based on ADF is obtained,

$$C_{re}(t) = \int d\alpha \int d(\alpha q_0)|F_{\lambda/\alpha^2}(\alpha q_t,0)F_{\lambda/\alpha^2}(\alpha q_0,0)| \exp\left[\frac{i}{\hbar}S_1(\alpha q_t,\alpha q_0,t) - i\frac{\pi}{2}M(\alpha q_0,\alpha q_t)\right], \tag{2}$$

which we call the renormalized AFC [3]. As in the case of the original AFC-II, this quasicorrelation function does not include an amplitude factor and does not suffer from divergence in

chaotic systems. Furthermore, due to the integration over α, the range of sampling space can be extended by making use of a set of reference trajectories and quantum interference between a reference and its copies is efficiently incorporated. Although in the above procedure we are showing the application to ADF only, just the same procedure is easily taken into other semiclassical wavefunctions such as those based on the semiclassical Feynman kernel [3].

In all numerical calculations of this work we have used geometrical evaluation of the Maslov index [4]. The Maslov index, which is an integer phase appearing in semiclassical wave functions, is the number of zero eigenvalues of the Jacobian determinant calculated along a classical trajectory. In our method we replace the Jacobi matrix (e.g.,, $\partial q_t/\partial q_0$) with a small discretized volume element ($\Delta q_t/\Delta q_0$) and monitor its change of orientation along a trajectory. This procedure avoids the calculation of the stability matrix, which becomes less reliable in a long time numerical calculation as well as time-consuming in a system with many degrees of freedom.

3 Results from some examples

3.1 Two-dimensional strongly chaotic system

As an example of the application of the renormalized AFC, we study the following rescalable Hamiltonian,

$$H = \frac{1}{2}p_x^2 + \frac{1}{2}p_y^2 + \frac{1}{2}x^2y^2 + \frac{0.01}{4}x^4 + \frac{0.01}{4}y^4, \tag{3}$$

which is known to be strongly chaotic and has no tori in any energy region.

Fig. 1(a) shows the spectrum from the original AFC-II using 500 trajectories. Although some of the semiclassical energies are in good agreement with the quantum values, the overall agreement is rather poor. This is not surprising in view of such a small number of trajectories sampled. In Fig. 1(b), the semiclassical spectrum is dramatically improved with the renormalized AFC. The noise in the spectrum is removed without practically increasing the number of classical trajectories. And energy levels covering a broader range are obtained with a single set of trajectories.

3.2 Two-dimensional H_2^+

Fig. 2 shows the spectrum for two-dimensional H_2^+ obtained with the renormalized AFC. Semiclassical energies are compared with the Born-Oppenheimer vibrational energies of H_2^+ in two dimensions. At this moment the number of classical trajectories sampled is very small (40 trajectories). However energy region including peak positions for the lower states are similar in both quantum and semiclassical cases.

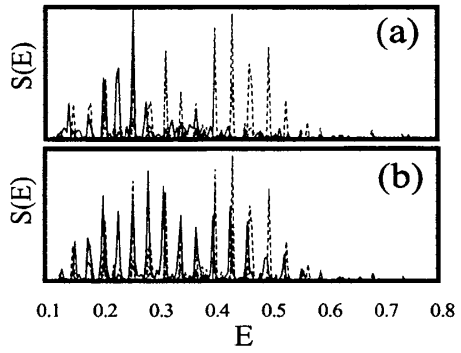

Fig. 1: Semiclassical energies of two-dimensional strongly chaotic system (solid curves) are compared with quantum energies (dashed curve). (a) Result from the original AFC. Overall agreement with the quantum result is poor. (b) Result from the renormalized AFC. Energy levels in a broader range have reproduced with scaling procedure.

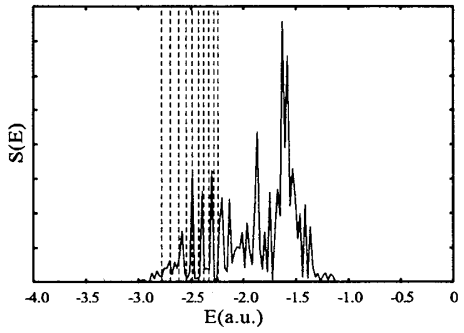

Fig. 2: Energy spectrum obtained with the renormalized AFC for two-dimensional H_2^+ (solid curve). For comparison, ten lowest Born-Oppenheimer vibrational energies are shown (dashed line).

4 Conclusion

We have developed a new way of semiclassical quantization for scale invariant systems such as Coulombic system. In this method interference between a trajectory and its copies effectively contribute to the energy quantization in scale invariant systems. In the application to two-dimensional H_2^+, energy levels near the vibronic ground state are obtained.

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